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by chemical and physicochemical methods, chapter 25
In: Yves Mouton (Eds), Organic Materials for
Sustainable Construction**

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Fabienne Farcas. Characterization of organic materials in civil engineering by chemical and physicochemical methods, chapter 25 In: Yves Mouton (Eds), Organic Materials for Sustainable Construction. Characterization of organic materials in civil engineering by chemical and physicochemical methods, chapter 25 In: Yves Mouton (Eds), Organic Materials for Sustainable Construction, WILEY, pp. 553-582, 2013, 10.1002/9781118616734 . hal-00876532

HAL Id: hal-00876532

<https://hal.science/hal-00876532>

Submitted on 25 Oct 2013

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Chapter 25

Characterization of organic materials in civil engineering by chemical and physicochemical methods

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From the domain of roads to the domain of construction, the organic materials used are very diverse (bitumens, paints, cements, etc), but studying their chemical structure and their composition generally uses the same analysis techniques.

Without claiming to be exhaustive, this chapter completes and brings up to date the presentation of chemical, physicochemical, physicochemical and thermomechanical properties previously offered [MOU 03] through research studying the chemical structure of basic organic materials and their additives, used in civil engineering. The original aspect of this work primarily lies in adapting methods and analysis conditions, the extension of their application domain and interpreting their results according to the nature of the material being analyzed (bitumen binders, anti-corrosive paints, organic admixtures used in cementing materials) and the problems posed.

25.1. Bitumen binders

For road technicians, there is no longer any doubt that a good number of setbacks encountered, during the implementation process as well as the bituminous mix lifespan, are related to the physicochemical and physicochemical characteristics of bitumens, and more generally, to the bituminous complex used.

Degradations observed are not systematic nor of the same amplitude for all the asphalt mixes. To try to explain the differences between the accused samples, one sought to define the characteristics chemical and physicochemical as precise as possible of the binders and to formulate the laws of evolution of these characteristics with time.

Confronted with the impossibility of characterizing a bitumen in its entirety, we have been led to base this on the model of colloidal structure [YEN 71], whose parameters seem sufficiently precise enough to describe or explain certain problems encountered during implementation, or later on during their working life. In this vein, research undertaken on bitumen binders was directed, on the one hand, towards a better knowledge of the chemical structure of bitumens whose performances are continuously improved by using new manufacturing processes and/or by adding various compounds and, on the other hand, towards a better comprehension of the phenomena involved in various ageing processes of bitumens.

The analytical techniques used for studying road binding agent are:

- silica rod chromatography (IATROSCAN);

- steric exclusion chromatography (SEC);
- Ultraviolet fluorescence spectroscopy (UVFS) and excitation-emission matrix spectroscopy (EEMS)
- Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES);
- Fourier Transform Infrared Spectroscopy (FTIR)

It is through these analysis techniques and, through considering the binders studied according to an order of increasing complexity in their chemical structure (pure bitumens, “special” bitumens, bitumens modified by polyphosphoric acids), that studies on bitumens are described. For each type of road binder, the chemical structure, then its evolution over ageing, are presented.

25.1.1. Pure bitumens

25.1.1.1. Chemical structure of pure bitumens

By adapting certain analysis methods makes it possible to highlight the colloidal structure suggested by Yen [YEN 71].

– *Silica rod chromatography (IATROSCAN)*, the technique which only takes into account the concentration of the generic bitumens families, independently of any quality standard, does not completely explain the mechanical behavior of bitumens. However, it is recognized that the bitumen consistency also depends on the interactions which exist between bituminous molecules and other molecules which intervene in the micellar equilibrium. To give an account of these interactions, we need to use a more adapted technique: steric exclusion chromatography (SEC) under “high-speed” conditions [BRU 87]. *High speed steric exclusion chromatography* applied to bitumens has made it possible to define a classification of three structure types, according to whether the bitumen consists of one, two or three populations. Taking into account diversity and the large number of samples, this technique has shown that bitumens which belong to the same class do not present the same quantities of molecular associations.

In order to better understand the structure and the molecular reorganizations responsible for the consistency of bitumens, we have made use of ultraviolet fluorescence spectroscopy (UVFS) and excitation-emission matrix spectroscopy (EEMS), which allow us to gain knowledge of the aromatic compounds, and to monitor their evolution during the binder’s ageing.

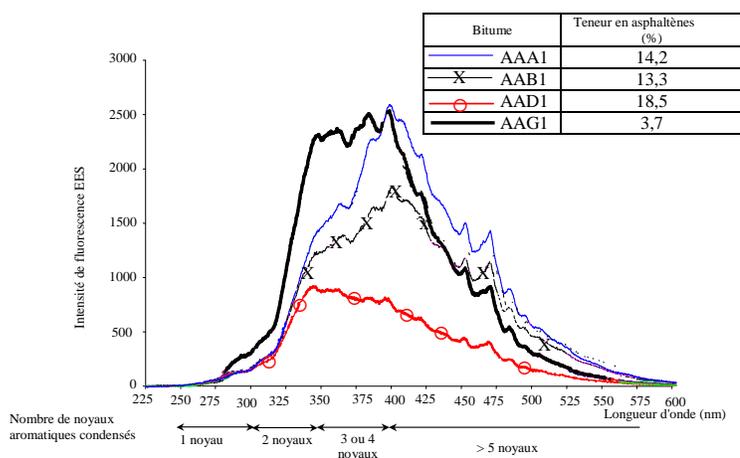


Figure 25.1. *Ultraviolet fluorescence spectroscopy (UVFS) in excitation-emission matrix spectroscopy (EEMS) of four bitumens from the SHRP*

Ultraviolet fluorescence spectroscopy (UVFS) in excitation-emission matrix spectroscopy (EEMS) mode was first developed in the framework of research on coals [KIS 92] before being applied to road bitumens [FAR 92a]. The interest of using the EEMS mode for bitumens which are complex mixtures, lies in simplifying the spectra, since each molecule is only represented by one single band. The information obtained in this way, then, lets us break away from majority tendencies.

The analysis of eight bitumens from the SHRP (*Strategic Highway Research Program*) [BUI 93, FAR 91, FAR 92a, SUC 94] showed that all bitumens had a comparable spectral print ranging from 250 Nm and 600 Nm with a maximum of 398 Nm (Figure 25.1). By using references to molecules found in relevant literature [VOD 78], it turns out that the condensation of bitumen aromatic cycles does not exceed 5 cores.

The reduced fluorescent intensity observed when the asphaltene quantity is increased can be explained by an extinction effect due to intermolecular interactions between the asphaltene molecules [FAR 92a].

The analysis of the three fractions obtained by “high-speed” SEC (one French bitumen and two Italian bitumens), shows that:

- The population fluorescence which is elected under the interaction peak is practically nil;
- The second population’s spectrum corresponds to the fluorescence compounds with 3,4 and 5 condensed cores;
- The third population, which corresponds to molecules with small molecular sizes, displays fluorescence in the zone of aromatic cores which are hardly condensed.

By this split analysis, it has been shown that the fluorescence spectral response complies with molecular size distribution. In the majority of cases, the bigger the bitumen’s interaction peak, the weaker the fluorescent intensity.

25.1.1.2. *Pure bitumen ageing*

This section describes the evolution of the bitumens’ colloidal structure under the influence of thermal shock during the coating process, simulated by the RTFOT standardized ageing test [AFN 00]. After this, there will be an ageing simulation for road bitumens by “oxygen bomb testing”, developed by the LCPC and validated by studying bitumens which have aged *in situ* (highway A8) [FAR 96].

25.1.1.2.1. *Ageing of bitumens used for road coating*

Let us remember that the leading cause for chemical ageing in bitumens is oxidation, caused by oxygen in the air which makes the bitumen harden [AFN 99]. The chemical analyzes carried out on three grade 35/50 French bitumens, and eight American bitumens, show that this hardening is a result of colloidal equilibrium evolution [FAR 92b, FAR 92c, FAR 96] :

- the analysis using IATROSCAN demonstrates an increase in asphaltene and resin content, as well as a reduced number of aromatics. The saturated content remains unchanged.
- the analysis using GPC shows an increase in the interaction peak, therefore an increase in asphaltene agglomeration;
- the analysis using FTIR reveals oxidation by the formation of carbonyl functions (increase in the absorption band to $1,700\text{ cm}^{-1}$) and sulfoxides (increase in the absorption band to $1,032\text{ cm}^{-1}$);
- the analysis using UVFS-EEMS undoubtedly shows a general reduction in the fluorescence intensity, particularly noticeable in the spectral zone of molecules composed of the most condensed aromatic structures [BUI 93, FAR 92a, SUC 94] inevitable due to rupturing and/or a recombination of large aromatic cores.

25.1.1.2.2. Ageing of road bitumens

In order to be able to predict the roadway sustainability, an *in situ* ageing simulation test was developed by the LCPC [FAR 96]. Its validity, considered from a physicochemical and structural point of view, is discussed here.

With the roadway temperatures rarely exceeding 50 to 60 °C in France [SUC 95], reproducing ageing effects of bitumens *in situ* requires a test which privileges oxidation at low temperatures, where the oxidation reactions are accelerated by an increase in oxygen pressure. For this, a standardized method for grease oxidation, the “oxygen bomb” test [AST 91], was adapted to bitumen ageing: a fine film (4 mm) of bitumen is oxidized in a vacuum at 50 °C and 70 °C under oxygen pressure of 2.2 ± 0.05 MPa [FAR 96].

We tried to reproduce the hardening kinetics of two French road bitumens, grade 35/50. For this, the evolution in the behavior of the bitumen by normal tests which tend to characterize its consistency at various temperatures was followed by measuring the softening point (TBA) and the penetration at 25 °C. Modifications of the chemical and colloidal structures were monitored by IATROSCAN and “high-speed” SEC methods.

Laboratory ageing conditions lead to:

- a reduced penetration and increased TBA, which is much larger when the temperature and the test duration are higher;
- an increased colloidal instability index and molecular associations which reveal an increasing bitumen structuration over the test duration.

In order to validate the accelerated ageing test, the modifications obtained after laboratory ageing tests were compared with those obtained from bitumen samples from highway A8.

The diagrams of penetration variation according to the TBA for two artificially aged bitumens from the experiment site on highway A8 (figure 25.2), show that the points obtained by oxidation in the laboratory at 50 °C and 70 °C follow the model (in a satisfactory way) represented by a hyperbolic function suggested by Brown [BRO 57], to describe *in situ* ageing.

With all the ageing factors (traffic, bad weather conditions, UV radiation, etc) not being taken into account, simulating structural modifications proved to be more difficult.

Comparing the variation between the I_c values taken from the road and the laboratory have shown that oxidation at 70 °C under an oxygen pressure of 2 MPa allows, for the two studied bitumens, us to simulate a structural state corresponding to different ages of *in situ* ageing. Here we find a difference in reactivity between the bitumens, undoubtedly the reason behind the previously shown differences in hardening.

On the other hand, variations in the percentage of the first chromatographic peak surface shows that the increase in the molecular associations induced by an oxidation temperature of 70 °C under 2 MPa of oxygen is not sufficient to simulate road ageing.

However, this study has enabled us to show that in the experimental field exploited by SEC, after the oxygen bomb ageing test over 96 hours at 70 °C under an oxygen pressure of 2 MPa, the dissociation kinetics of the dissociable asphaltene species when in solution is close to that for the same bitumen aged for 84 months on the road [FAR 96].

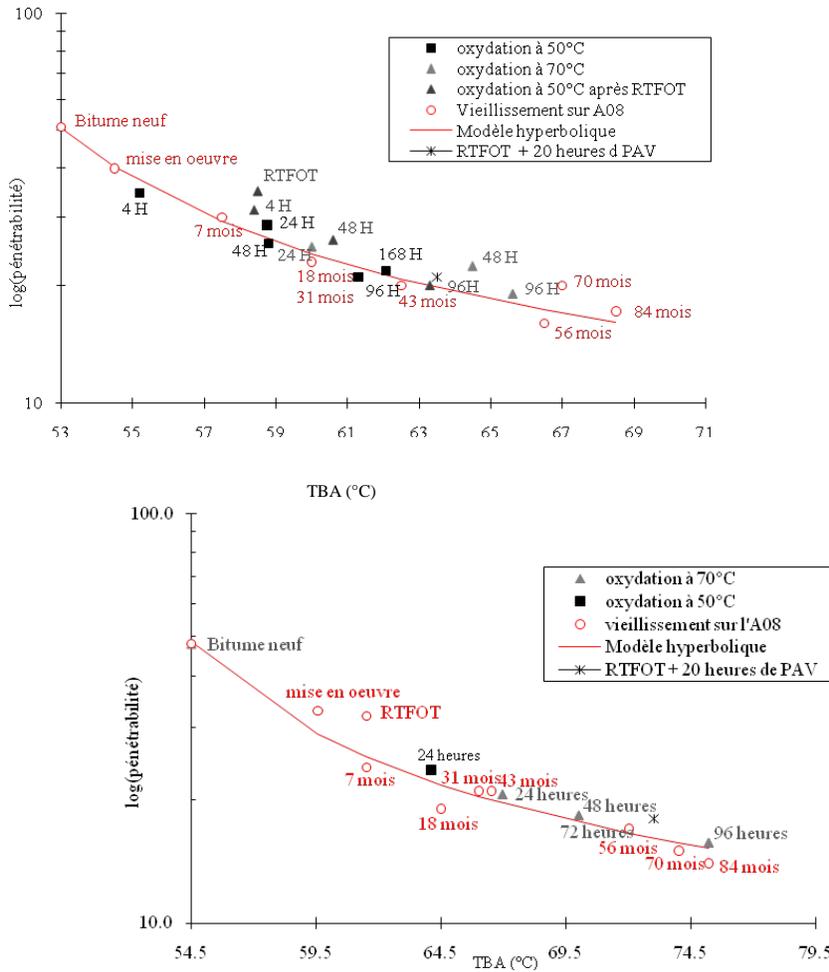


Figure 25.2. Variation of the penetrability logarithm according to the softening point of two same grade bitumens aged on the road and in the laboratory

25.1.2. Special bitumens

In order to fight against the tracking, the manufacturers have developed “special” bitumens. While making extensive use of consistency criteria (penetration and TBA), the European specifications [AFN 99] leave behind them the fear of premature crack growth on the roadways.

However, the observations carried out on certain roads made using this type of binder show good behavior in the bitumen mix during winter temperatures [MAR 99]. To understand the particular behavior of these new bitumens, the same analytical techniques as for pure bitumens have been used.

Moreover, in order to distinguish the different bitumens studied, it was interesting to determine Ni, V, S and P content, which represent a way of distinguishing bitumens according to their origin, or even the method used to make them. The dosage of these elements is decided on according to an elementary analysis method by ICP-AES, developed by the LCPC, which enables us to analyze bitumens simply by putting them into an emulsion [DRU 00].

Four “special” bitumens and a “traditional” bitumen of the same grade (35/50), considered here as a reference bitumen, were studied. The evaluation and the comparison of ageing effects on the chemical structure of the “special” bitumens were performed by considering various stages of ageing.

25.1.2.1. Elementary analysis by ICP-AES spectrometry

The values for Ni and V content, characteristic of crude oil bases, (Table 25.1), show that the studied bitumens are made by using three oils, all coming from different origins:

- “special” bitumens A and B come from similar oils;
- “special” bitumens C and D are made from oils with close origins;
- “traditional” bitumen R comes from a third oil source.

The sulfur contents prove to be comparable for the five bitumens (Table 25.1). The “anti-tracking” performances of the “special” bitumens, therefore, cannot be attributed to the addition sulfur, which (by a vulcanization process), gives them a higher modulus.

	Ni	V	S*	P
Wavelength of emission bands	231.60 nm	290.88 nm	181.98 nm	214.91 nm
Bitumen R	67.7 ppm	234.0 ppm	3.0 %	Not detected
Bitumen A	18.1 ppm	76.4 ppm	3.6 %	Not detected
Bitumen B	14.8 ppm	70.1 ppm	3.2 %	Not detected
Bitumen C	32.0 ppm	116.0 ppm	4.4 %	0.4 ppm
Bitumen D	31.4 ppm	234.0 ppm	3.0 %	Not detected

* The sulfur contents are expressed in mass percentages.

Table 25.1. Ni, V, S and P contents in four “special” bitumens (A, B, C, D) and “traditional” bitumen (R) determined by ICP-AES

25.1.2.2. Determining the structure state by using IATROSCAN

Strong asphaltene contents lead to high of I_c values (Table 25.2), indicating that “special” bitumens are extremely structured, in comparison to traditional bitumen.

Bitumen	Saturated (%)	Aromatic (%)	Resins (%)	Asphaltene (%)	I _c	Asphaltenes precipitated by n-heptane (%)
R	7	48	30	15	0.28	10.2
A	8	49	24	20	0.39	19.3
B	9	43	26	21	0.44	19.5
C	6	43	25	26	0.48	22.6
D	8	42	28	23	0.45	18.7

Table 25.2. Separation into generic families by IATROSCAN and asphaltene content precipitated by N-heptane

Generally, the highly structured bitumens are oxidized bitumens, rich in oxygenated functions. In order to evaluate the bitumen's oxidation state, IRTF spectrometry represents an analysis technique which is especially able to proportion and determine the nature of the functions present in a compound.

25.1.2.3. Determining oxidation state by IRTF spectrometry

Analyzes by using IRTF spectrometry show that bitumens, all grades together, have the same chemical functions. These spectra are simple and reveal that bitumens mainly consist of aliphatic and aromatic hydrocarbons. Their functionality is primarily related to the presence of carbonyl functions (C = O) towards 1,700 cm⁻¹ and sulfoxide (S = O) towards 1,032 cm⁻¹, revealing the binder's oxidation state. Evaluation their content represents a way of distinguishing bitumens between them and, as we will see further on, and evaluating their susceptibility to ageing.

This technique enabled us to show that the structure of "special" bitumens can be attributed to a high carbonyl content. This conclusion lets us consider that the manufacturing process of these bitumens includes a "blowing" stage. The oxygenated functions of bitumens are the base of molecular associations and generate complex structures which define the bitumens' colloidal structure. The carbonyl function content highlighted by IRTF testing induces differences in the colloidal structures between bitumens, which we try to visualize by using "high-speed" SEC methods.

25.1.2.4. Determining the colloidal structure by using "high-speed" SEC

The results for quantifying each chromatographic population (Table 24.3), performed using a program which allows chromatogram deconvolution in three Gaussians, confirm the high structuring of "special" bitumens. It is important to note here that not all "special" bitumens present the same structure (bitumen D is approximately three times less structured). They are, therefore, not all manufactured by the same process.

Commentaire [ISTETrans1]: En trois Gaussiennes?

The application of different analysis techniques leads us to conclude (in a univocal way) that the "special" bitumens are structured bitumens, obtained by processes which involve oxidation reactions. In order to understand this unexpected behavior during the ageing of these bitumens, the evolution in their chemical structure, during the mixing process and when finally on the road, is studied in the following section.

Bitumen	Agglomeration (%)	Micelles (%)	Molecules (%)
R ("traditional")	0.5	8.5	91.1
A	7.2	10.3	82.5
B	5.9	11.7	82.4
C	6.9	21.8	71.4
D	2.0	29.5	74.6

Tableau 25.3. Contents of molecular associations and molecules isolated from "traditional" bitumen and from the four "special" bitumens

Modifications, over time, of the chemical structure of the four "special" bitumens are studied by two artificial ageing tests:

- RTFOT, ageing stage during aggregate coating;
- RTFOT, followed by 20 hours of PAV (pressure ageing vessel), *in situ* ageing stage

The two stages of ageing considered lead to an increase in the asphaltene content of the "special" bitumens identical to that for "traditional" bitumen. Similarly, the increase in the I_c value is comparable for all bitumens.

Oxidation during ageing results in the formation of sulfoxide and carbonyl functions, more or less noticeable according to the bitumen: bitumens A and B appear to be the most oxidizable. In parallel, these are the two bitumens which have the greatest sensitivity to cold crack growth. The two other bitumens oxidize less, where the oxidability of bitumen D is comparable to the reference bitumen.

The formation of oxygenated functions contributes to the creation of molecular associations. However, it cannot be directly related to the bitumens' structuring (formation of molecular associations) because it does not take into account other phenomena, such as polycondensation reactions.

The "high-speed" SEC techniques, performed at the two stages of ageing on the bitumens, shows that molecular associations of the "special" bitumens increase much less than those for "traditional" bitumens. This observation is not surprising, seeing as we know that a structured bitumen is not very ageing sensitive.

The differences in manufacture processes, and the low contents of metal may be the parameters which lead to differences in modification of the colloidal structure observed between "special" bitumens.

25.1.3. Polyphosphoric acid (PPA) modified bitumens

Polyphosphoric acid (APP) modified bitumens are used, particularly in the United States, to improve the properties of bitumens with regard to the SUPERPAVE (*Superior Performing Asphalt Pavements*) reference specifications [ASP 95]. The effect of adding APP to bitumens is similar to the effect induced by the blowing process: lower penetration, higher viscosity. In addition to good ageing resistance, the advantages of such an attribute, in relation to blowing, are low costs and a minor incidence on behavior at low temperatures [DEF 95].

APP modified bitumens have not only improved mechanical properties, but also a better resistance to deoiling from water [ASP 01]. The few elements which we know today on the physicochemistry of APP modified bitumens [BIS 01, HO 01], do not enable us to explain these property modification, and the action mode of these acids still

remains widely misunderstood. Research on the chemical structure of APP modified bitumens appears all the more necessary, as some APP modified bitumens do not display the improvements described above.

25.1.3.1. Basic materials and usual mixture characteristics

In order to exalte the characteristics of APP modified bitumens, we have chosen to carry out work on mixtures of bitumens modified by 2 % APP - the rates usually used in the USA being around 0.9 to 1.2 %. The polyphosphoric acid introduced to the mix is a polyacid with the supposed composition: H_3PO_4 (54 %); $H_4P_2O_7$ (39 %); $H_5P_3O_{10}$ (7 %).

Three bitumens of different origins which respond differently to the modifications were selected for this study (Table 25.4).

Bitumen	Crude bitumen origin	Improvements in mechanical properties by adding 1 % APP
Av	Venezuela	Strong
Bm	Mexico	Average
Cc	Canada	Nil

Table 25.4. Origin and behavior with the addition of APP to the studied bitumens

Whatever the bitumen considered, penetration measurements at 25 °C show that polyphosphoric treatment makes the basic bitumen lose a penetration grade. This criterion is more important for the Av bitumen, which is distinguishes itself from both the other bitumens by a particularly strong increase of TBA after RTFOT [SUC 03]. Therefore, bitumen Av does not come into the framework of current European specifications [AFN 99]. In parallel, this bitumen, stated as being that which sees a larger improvement after adding the APP, also seems to be the most reactive in terms of its usual characteristics.

25.1.3.2. Chemical and structural analyzes

The elementary ICP-AES analyzes of unmodified bitumens means that we can distinguish bitumen Av by a strong vanadium content. With the exception of this characteristic, the three bitumens appear identical.

Adding APP results in a large increase in the asphaltene precipitated by N-heptane content (approximately 6 %) which should give a harder bitumen, than the one observed (penetration of 39/10e mm). As an indication, a pure bitumen with a high asphaltene rate (23 %) generally has a penetration lower than 20/10^e mm. To explain these contradictory values, we propose the hypothesis that the APP reacted with the aromatic asphaltenes and the resins to form phospho-aromatic insoluble asphaltenes in normal heptane, but soluble in cycloaliphatics.

Separating the bitumens into generic families by using IATROSCAN indicates:

- for bitumen Av, a reduction in the asphaltene content by 0.5 %; an increase in the aromatic content by 27 % and a reduction in the resin content by 2 %;
- for bitumens Bm and DC, a reduction in the asphaltene content by approximately 3 %;
- for bitumen Bm, a reduction in the aromatic content by 3.6 % and an increase in the resin content by 0.8 %;
- for bitumen Cc, a small variation of the aromatic content, and an resin increase by 3.6 %.

The increase in the I_c values of bitumens Bm and Cc leads to a structuration in the bitumens after modification. This conclusion is also verified by rheological tests, which show that the elastic nature of the binding agent increases with the APP content [ORA 04].

Separating the bitumens into generic families by using IATROSCAN methods does not enable us to find the large variation in the content of insoluble asphaltenes in N-heptane after modifying the basic bitumen. This means that the products coming from the APP and bitumen reaction are separated with the other generic families. The hypothesis of phospho-aromatic soluble asphaltenes in toluene and chloroform therefore seems plausible.

The “high-speed” SEC analyzes of the three bitumens present a reduction in the quantity of agglomerated asphaltene after modification. Used as an additive, added in the bitumens in small quantity (1 %) in the majority of cases, APP destroyed the bitumens’ colloidal structure [DEF 95]. The APP appears to be an asphaltene dispersant. This result, which is *a priori* surprising if we take into account the bitumen structuring demonstrated by the I_c values and rheological tests, is still favorable to the hypothesis on phospho-aromatic components formation which are compatible with resins and bitumen aromatics.

To conclude this study, reducing the concentration of species with large molecular sizes, as can be detected by SEC methods, promotes the formation of phospho-aromatics which disperse the asphaltenes in the maltene environment. The results of separating into generic families and the asphaltene contents agree with this hypothesis.

25.2. Anti-corrosive paints

The aim of the study presented here was to determine ageing indicators sensitive enough to allow for intervention before constructions and structures degrade and require heavy, expensive repairs.

Thanks to the sensitivity of current analytical techniques, applying them to the study of a material’s chemical evolution represents a method of detecting paint degradation at an early stage. A bibliographical study showed that infra-red spectrometry (transmission, specular reflection, diffuse reflection, transreflexion and attenuated total reflection (ATR)) [DEF 98, CHE 00, IRI 01, ISA 72, LEM 98, NGU 87, PER 00, WER 97] is an interesting technique for studying the chemical modifications of polymers during ageing. It is, then, this method which was retained for naturally detecting significant indicators of chemical modifications in the finishing coat of four coating systems (chlorinated rubber, urethane alkyd, polyurethane and acrylic urethane) aged naturally for 12 months Florida, i.e. under particularly aggressive conditions (UV radiation, heat, moisture and marine environment) [FAR 01a, FAR 03].

The modifications of the binding agent’s chemical functions are studied by IRTF:

- in transmission mode: this infra-red analysis mode requires the finishing coat surface to be recovered by manual scraping;
- in attenuated total reflection mode (ATR): this analysis mode enables a study on the paint surface between 650 cm^{-1} and $4,000\text{ cm}^{-1}$; for a sample whose refraction index is 1.5, the infra-red beam has a penetration depth ranging between $0.6\text{ }\mu\text{m}$ and $4.8\text{ }\mu\text{m}$ [PER 00]. Using an ATR microscope means that we can analyze a small surface (infra-red spot size: $60\text{ }\mu\text{m}$), therefore establishing sufficient contact between the internal reflection crystal and the often rough film, especially after an ageing test.

The part of the infra-red spectrum located below $1,500\text{ cm}^{-1}$ is highly characteristic of a molecule, but sometimes proves difficult to interpret. Moreover, for products containing mineral fillers, which is the case for paints, the absorption bands of the organic compounds are masked by those of the mineral compounds, which have intense absorption bands below $1,200\text{ cm}^{-1}$ [FAR 01b]. This is why, in the majority of the cases, we were interested in the part of the IRTF spectrum ranging between $2,000\text{ cm}^{-1}$ and $1,500\text{ cm}^{-1}$ which corresponds to an infra-red absorption zone whose interpretation is reliable and unambiguous.

The IRTF spectra of different colored finishing coats for a system coming from the same manufacturer proved to be identical. The pigments, added in small quantities into the mixtures, do not appear on the spectra. Moreover, for a given binder type, the same IRTF spectra modifications for aged paints were noticed. From this, we can confirm

that, independent from the problem of changes to the color and gloss of the finish, the pigment does not influence the paint's chemical ageing nature.

Certain paint binding agent have common infra-red absorption bands. Thus, an IRTF study is conducted by distinguishing two groups of binding agent:

- chlorinated rubbers;
- polyurethanes, acrylic-urethanes and urethane-alkyds.

25.2.1. Ageing of chlorinated rubber binders

The list of the main absorption bands observed on the IRTF spectra for analyzed chlorinated rubber paints is given in Table 25.5.

The comparison of IRTF spectra for witness, aged, chlorinated rubber paint (Figure 25.3) does not make it possible to directly highlight the intrinsic chemical modification the binder. Indeed, the double characteristic of the C-Cl bonds, between 600 cm^{-1} and 700 cm^{-1} , is masked by talc absorption ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) to 669 cm^{-1} .

Wave number (cm-1)	Chemical functions in vibration
3 675	v (OH) (talc)
2 966-2 851	v (CH ₃)
2 923	v (CH ₂)
1 731	v (C = O) ester
1 600	Aromatique cycle
1 444	δ (CH ₂)
1 370	δ (CH ₃)
1 017	δ (Si-O) (talc)
669	v (Si-O) (talc)
534	v (Si-O) (talc)
465 et 451	v (Si-O) (talc)

Table 25.5. Attribution of the main absorption bands read on IRTF spectra, chlorinated rubber paints (v: elongation vibration; δ: strain vibration)

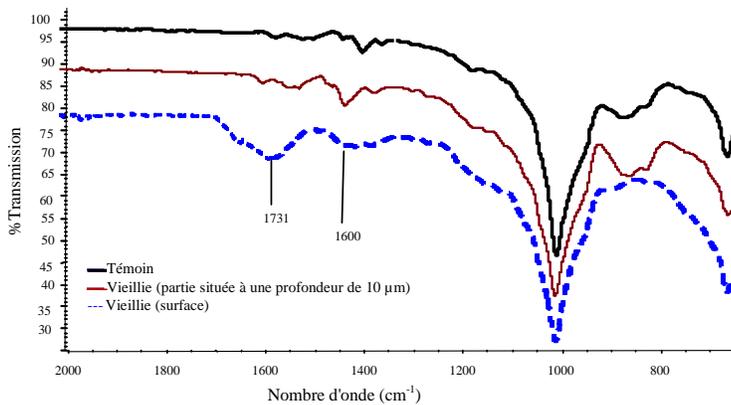


Figure 25.3. IRTF spectra in ATR mode, the surface parts of chlorinated rubber paint, aged naturally for 12 months in Florida, and the part located at a depth of approximately 10 μm in the aged system

However, we can see a modification in the IRTF spectrum of the paint, aged by an increase in the absorption bands to $1,731\text{ cm}^{-1}$ and $1,600\text{ cm}^{-1}$ which can be explained by two phenomena:

- migration of the plasticizer towards the surface, phenomenon behind polymer deplasticization [MAT 96];
- oxidation of the chlorinated rubber binder by photochemical degradation mechanisms [VER 84, WIL 97].

The IRTF spectrum of the part located at a depth of $10\text{ }\mu\text{m}$ is identical to that of the witness (Figure 25.3), which shows that ageing symptoms are no longer observed at a binder depth higher than $10\text{ }\mu\text{m}$.

25.2.2. Ageing of polyurethane, urethane-acrylic and alkyd-urethane paint binders

The main absorption bands characteristic of polyurethane, urethane-acrylic and urethane-alkyd paints are reported in Table 25.6.

Wave numbers (cm^{-1})			Attributions
Polyurethane	Urethane-acrylic	Urethane-alkyd	
1 730	1 730	1 732	ν (C = O) ester
1 689	1 690	674	ν (C = O) urethane
1 634	1 648	1 652	ν (C = O) secondary amide
///	///	1 623	ν (C = O) third amide
1 524	1 520	1 550	δ (N-H) and ν (C-N) secondary amide
Absent	Absent	Absent	ν (C-O) ester

(ν : elongation vibration ; δ : strain vibration)

Table 25.6. Attribution of the main absorption bands of the IRTF spectra, polyurethane, urethane-acrylic, and urethane-alkyd paints

Differences in formulation explain the absence of certain characteristic absorption bands which are observed for certain paints. It is there the IRTF spectrum of urethane-alkyd binder (Figure 25.4) which was used as a basis for describing the induced chemical modifications by the natural ageing on the three types of paints studied. According to the bands present on the original spectrum, we observed five chemical modifications:

- stretching of the ester carbonyl band towards $1,732\text{ cm}^{-1}$ with formation of a **shoulder** towards $1,800\text{ cm}^{-1}$;
- reduction in the urethane carbonyl band towards $1,674\text{ cm}^{-1}$;
- reduction in the intensity of secondary amide carbonyl bands towards $1,653\text{ cm}^{-1}$;
- increase in the tertiary amide band towards $1,623\text{ cm}^{-1}$;
- increase in the surface area ranging between $1,500\text{ cm}^{-1}$ and $1,680\text{ cm}^{-1}$.

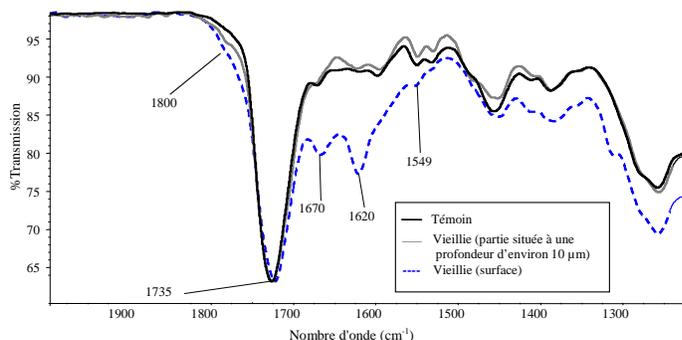


Figure 25.4. IRTF spectra in ATR mode for the surface coats of urethane-alkyd paint witnesses, aged naturally over 12 months in Florida, and located at a depth of approximately 10 µm of the aged paint

The retained spectral modifications correspond to a photo-oxidation mechanism of the polyester-urethane polymers [WIL 97]. Stretching the carbonyl band, and the appearance of a shoulder at 1,800 cm^{-1} characterize an oxidation in the binder, by the formation of **carboxyl carbonyls** and acetyl urethane (-CO-NH-CO-O-). The reduction in the urethane carbonyl band to 1,674 cm^{-1} highlights urethane degradation. The reductions in the secondary amide bands to 1,653 cm^{-1} and 1,550 cm^{-1} are explained by the rupturing of C-N bonds, observed in polymers comprising of amide groups, which leads to the formation of a precursory radical of an amide which corresponds to the band at 1,623 cm^{-1} [ROG 85].

The IRTF analyzes for the paint located at approximately 10 µm under the exposed surface show that they are different according to the binding agent:

- for polyurethane paint, the IRTF spectrum shows that at 10 µm depth, the binder tends to find the same chemical structure as the witness; however, the ester band at 1,730 cm^{-1} , still masks the urethane-carbonyl band;
- for the acrylic-urethane paint, we note the absence of the mass width, which includes the ester carbonyl bands (1,730 cm^{-1}) and urethane bands (1,684 cm^{-1}). On the other hand, although less intense than on the witness spectrum, the band at 1,798 cm^{-1} , (characteristic of calcite), becomes visible again;
- for the urethane alkyd paint, the IRTF spectrum performed at a depth of 10 µm is identical to that of the witness plate.

In conclusion the IRTF analyzes of five paint systems (each one in several colors), witnesses, and aged for 12 months in Florida, let us demonstrate that:

- the pigment does not influence ageing ;
- whatever the nature of the binder, natural ageing causes an oxidation for the constitutive polymers;
- for the four paint system studied, the IRTF analyzes in transmission mode, as in ATR mode, enable us to highlight ageing indices related to a polymer's photo oxidation phenomenon:
 - the ageing of rubber chlorinated paint results in an increase in the carbonyl band towards 1,735 cm^{-1} and in the band at 1,600 cm^{-1} ;
 - the three other types of paint studied have the same chemical functions:
 - esters (towards 1,735 cm^{-1});
 - urethane carbonyls (towards 1,674 cm^{-1});
 - secondary (towards 1,652 cm^{-1} and 1,550 cm^{-1}) and tertiary amides (towards 1,623 cm^{-1}).

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By considering all the chemical modifications detected in this binding agent made of urethane and ester functions, it is possible to remove ageing indices which correspond to:

- formation of carbonyl functions;
- degradation of urethane functions;
- degradation of secondary amide functions;
- formation of tertiary amides.

Used in ATR mode, IRTF spectrometry reveals that, for most cases, ageing only affects the surface part of the paint.

25.3. Organic adjuvants in cementing materials

As previously seen, in the third part of this work, rheological admixtures in cementing mixtures represent an undeniable advantage for implementing these products, whether it is a question of concretes, mortars or grout. However, we may note problems of premature hardening when using water reducing plasticizer type admixtures, superplasticizer, grout admixtures for pre-stressing, etc. To understand the reasons for these phenomena, studying the interactions between the superplasticizer molecules and the cement grains was necessary.

The studies described here first of all considered, from the point of view of detecting “traditional” superplasticizers in hardened concretes and, secondly, from the point of view of characterizing the “new generation” superplasticizers in a new type of concrete, first seen in France in the 1990s, high-performance concretes (HPC) or self-leveling concretes (SLC).

25.3.1. Evolution of “traditional” superplasticizers in hardened cement pastes

Questioning the presence of admixtures in disorders which may appear on building sites (premature hardening, too long setting times, lack of mechanical resistance, etc) requires us to establish their responsibility in a univocal way.

The first stage of this work consisted of leading a physicochemical characterization of the base superplasticizers, which is necessary before approaching the study of the future of superplasticizers extracted from cement pastes hardened in a second stage [MAR 97].

Three samples belonging to the three most frequently used superplasticizer families were studied:

- polynaphtalene sulfonates (PNS);
- polymelamine sulfonates (PMS);
- lignosulfonates (LG).

25.3.1.1. Characterization of superplasticizers

The IRTF spectra for each admixture enable us to differentiate the families between them, without a distinction between products of the same family being possible. On the spectra for each family, we will only retain the characteristic infra-red absorption bands in Table 25.7.

The IRTF analyzes are not sufficient for a complete chemical characterization of the admixtures. Indeed, the number of sulfonate groups and the polymer sizes are mainly responsible for cement particle dispersion when in contact with mixing water [AFN 94, BAS 86]. The sulfonate group numbers were therefore determined by an acid-

alkaline dosage and by sulfate ash formation, according to norm NF T 60-143 [FER 86]. These two methods, which lead to similar results, show that the number of sulfonate groups for PNS and PMS are comparable, and approximately 60 to 70 % higher than those for LG [MAR 97].

Chemical family of superplasticizer	Vibration frequencies (cm-1)	Chemical vibration	Chemical function
PNS	1 600 and 1 500	ν (C=C)	aromatic cycle
	1 444	δ (CH)	ethyl (CH ₂)
	1 356	δ (CH)	methyl (CH ₃)
	1 184-1 120 and 1 034	γ (S=O)	sulfonate
	829.752 and 562	γ (CH)	Aromatic substitution
	682 and 622	γ (S=O)	sulfonates in the PNS
PMS	1 555 and 1 485	ν (C=N)	triazine cycle
	1 360	δ (CN)	amine
	186 and 1 044	ν (S=O)	sulfonate
	810	ν (C=N)	Triazine cycle
LG	1 600 and 1 500	ν (C=C)	aromatic cycle
	1 604	ν (CO)	carboxylic (COO ⁻)
	1 210 and 1 040	ν (S=O)	sulfonate
	651	δ (S-O)	sulfonates in the LG

ν : elongation vibrations; δ : strain vibrations; γ : swinging vibrations.

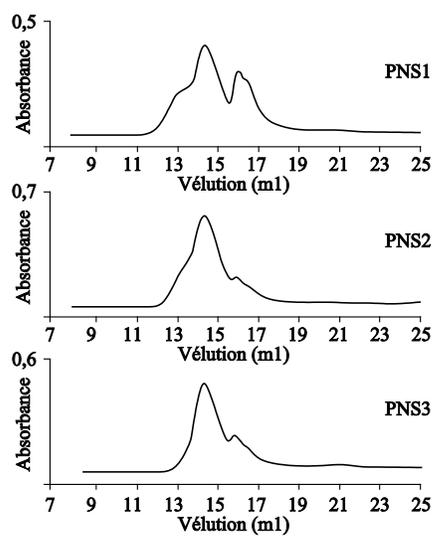
Table 25.7. *Infra-red absorption bands characteristic of superplasticizers*

The best adapted technique for evaluating the size of macromolecules such as superplasticizers, is steric exclusion chromatography (SEC).

While using work by Basile and Ferrari [BAS 86, FER 86] as a starting point, we carried out the separation using two chromatographic columns, filled with a sulfonic divinylbenzene type gel, Shodex Ionpak KS 803 and KS 804.

In order to eliminate ionic exclusion, we used one eluent acid, made up of an orthophosphoric acid aqueous solution 10⁻¹ M (acid used for extracting admixtures in cementing materials), adjusted to a pH level of 2 (at this pH, the anionic sites of polymers, and the chromatographic gel are in protonic form). Under these analysis conditions, we were not able to obtain a satisfactory separation of the LG.

On the other hand, the chromatograms obtained for the PNS and PMS (Figure 25.5) show that within the same chemical family, the admixtures do not present the same distribution in molecular sizes.



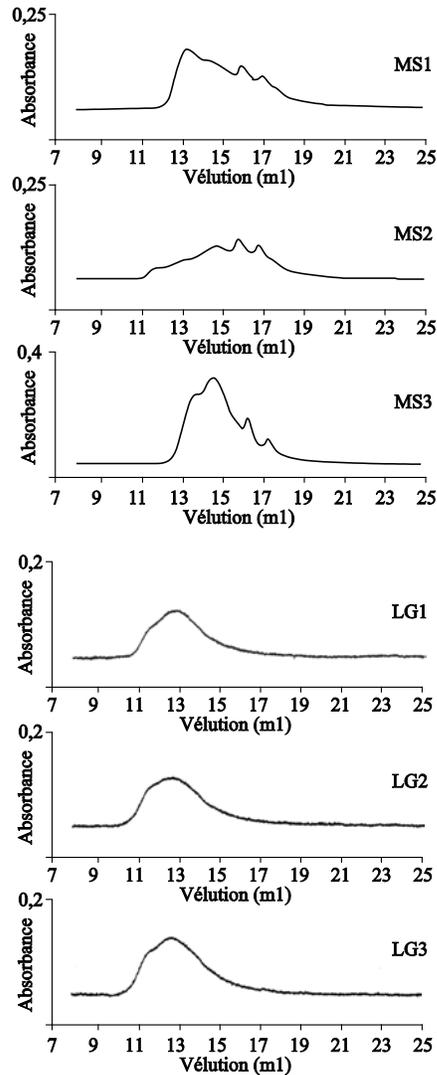


Figure 25.5. Chromatograms of commercial PNS and PMS

25.3.1.2. Detection and dosage by SEC of a PNS and a PMS extracted from hardened cement pastes

Among all the analysis techniques considered (mass spectrometry, NMR, capillary electrophoresis), the steric exclusion chromatography in aqueous phase proved to be most interesting for studying “traditional” superplasticizers, extracted from hardened cement pastes (HCP) [MAR 97].

The solutions chromatograms for extracting of HCPs aged for 2 years in a laboratory, containing various quantities of PNS and LS, show no difference in the distribution of molecular mass compared to the pure product. In the same way, the surface calculation of the chromatograms highlights that the selected extraction method, followed by a SEC analysis, enables us to find up to 80 % of the admixture mass introduced into the cement paste.

The detection and dosage of the polymelamine sulfonates (PMS) by SEC, extracted from HCPs, proved impossible under the selected analysis conditions, because this molecule is subjected to hydrolysis in basic environment. The polymelamine formed is insoluble in the interstitial environment [MAR 97]. Indeed, we have shown that the chromatographic response for a PMS solution to a pH level of 13.6 (pH of a young age cement), decreases by approximately 90 % in one week. With the PMS being comprised of molecules which contain nitrogen atoms, the dosage of total nitrogen by the KJELDAHL method, according to a procedure describe in the norm NF X 31-111, proved to be a relevant method for dosing 75 % PMS in hardened cement pastes, after extraction following 21 months of natural ageing in a laboratory.

At the end of this study, we have a dosage method for traditional superplasticizers in cementing materials [WIT 01] as well as a testing method which enables us to characterize the evolution of these admixtures.

25.3.2. New generation admixtures

Since 1990, a new type of concrete appeared on the French market: self-leveling concrete (SLC). These special concretes are defined as being fluid concretes, which stay in place just by gravitational effects, without need for vibration, even in very complex formwork. [SED 95]. The installation of such concretes requires the addition of particularly active “new generation plasticizers” which, while being added in low doses, ensures a good spreading of the material at young age.

In order to identify the active functions of this new superplasticizer used in SLC, a certain number of characterization tests according to standardized procedures were carried out on ten commercial “new generation superplasticizers” [FAR 07]. IRTF spectrometry has proved to be best adapted method distinguishing admixtures according to functional groups which ensure their fluid effect.

This technique, compared to data reported in literature on the subject [CAL 98, HAS 99], has made it possible to characterize superplasticizers, like methacrylic ester copolymers or negatively charged acrylics (according to the environment where they are located) on which the poly(ethylene oxide) (uncharged) or poly(ethylene oxide) groups are fixed. The main absorption bands present on the IRTF spectra of analyzed admixtures are reported in Table 25.8.

vibration frequencies (cm ⁻¹)	Chemical vibrations	Chemical groups
3 440	v (OH)	residual water and hydroxyls
2 800-3 000	v (CH) v (CH ₂) v (CH ₃)	Methines methylenes methyls
1 731 and 1 729	v C=O	esters*
1 719	v C=O	carboxylic acids
1 581 to 1 568	v (O=C-O) ⁻	carboxylate
1 456	δ CH ₂	methylenes
1 351	δ CH ₃	methyls
1 250	v CO	ether (ethylene glycol)

ν :	1 102	ν C-O	ether oxyde	Vibrations d'élongation ; δ :
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Strain vibrations
* Only for some polycarboxylates

Table 13.8. Attribution of the main absorption bands of IRTF spectra for (poly)ethylene polyoxide and polycarboxylates superplasticizers

IRTF spectrometry has made it possible to highlight the fluidifying chemical functions of “new superplasticizer” which are ensured by poly(ethylene polyoxide) chains grafted onto a polymer which contains carboxylate groups [CAL 98, HAS 99], meaning poly(ethylene polyoxide) chains which generate steric repulsions, therefore prolonging the fluidifying effect. The presence of carboxylate and carboxylic acid groups in acrylate and methacrylate type superplasticizer in the does not exclude the presence of ester groups [DUF 98, YAM 00]. Indeed, these functional groups are sometimes highlighted by the presence of absorption bands at $1,731\text{ cm}^{-1}$ and $1,729\text{ cm}^{-1}$ for admixtures. These absorption bands for the ester functions mask the bands which are characteristic of carboxylic acids.

25.4. Conclusion

Although a direct relationship between the rheological or mechanical characteristics of materials and their chemical structure cannot always be established, studies undertaken today show that a modification in material behavior is always accompanied by a modification in chemical structure. The chemical characterizations described in this chapter therefore represent important studies for the understanding of the materials' use properties.

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